

Supporting Information

Quantum phenomena in nanomaterials: coherent superpositions of fine structure states in CdSe nanocrystals at room temperature

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S1. Theoretical methodologies

S1.1 Parameters and model details for the fine structure

In the EMA, the single particle electronic wave functions, for the hole and the electron, $\psi_{e/h}^E(\mathbf{r})$, are written as a product of a radial envelope and a Bloch function $\psi_{e/h}^E(\mathbf{r}) = R(\mathbf{r})u(\mathbf{r})$. The Bloch functions are taken at the Γ point of the Brillouin zone and defined over one unit cell.

In bulk CdSe, the conduction band is made of s-type orbitals of the Cd atoms and has a symmetry Γ_6 in the T_d group and the Γ_8 valence band is made of p type orbitals of the Se atoms. The electron wave functions of the ground state of the electrons in the conduction band can be written as

$$\psi_{sz}^e(\mathbf{r}) = R^e(\mathbf{r})u_{1/2,sz}^c(\mathbf{r}) \quad (1)$$

where the Bloch function $u_{1/2,sz}^c(\mathbf{r})$ is of s ($l=0$) symmetry and the spin of the electron $s=1/2$, with projections $sz = \pm 1/2$. We consider only the ground state envelope function for the electron, which is also of $l=0$, that is of s symmetry. The electron state is labeled $1S_e$ where S stands for the L value of the radial wave function and is a two-fold degenerate state with a total angular momentum $S = 1/2$ and $S_z = \pm 1/2$.

The structure of the single particle states of the hole of the valence band is more complex. Due to the strong spin orbit coupling in the bulk between the orbital angular momentum of the p shell and the spin of the hole, spin is not a good quantum number for the hole Bloch function.^{1,2} The manifold of states is further split by the exchange coupling and the crystal field coupling that can lead to band mixing between hole functions of different orbital quantum number.

Taking into account the strong spin orbit coupling in the valence band of bulk CdSe, two values of the total hole angular momentum, $j = l \pm s_h$, for the Bloch function are possible, $j = 3/2$ and $j = 1/2$. In the simple model that we use, we neglect band mixing and take $L = 0$ for the angular momentum of the radial envelope function, so that J_h , the total angular momentum of a hole state is equal to that of the hole Bloch function. We therefore have two sets of single particle wave functions for the hole: the lower four degenerate $J = 3/2$ branch (heavy and light hole states), with M_J projection values, $-3/2, -1/2, +1/2$ and $+3/2$, and the higher two fold degenerate $J = 1/2$ band with projections $M_J = -1/2$ and $+1/2$.

When combining the angular momentum values with the electron spin, one new quantum number, the parity quantum number $F = J \pm S_e$ is obtained, which leads to a 8 degenerate manifold for the $J = 3/2$ band with F values 1 and 2 and projections $F_z = 0, \pm 1$ for $F=1$ and $0, \pm 1$ and ± 2 for $F=2$ and a 4 degenerate manifold for the $J = 1/2$ band, $F=0$ and $F = 1$ with $F_z = 0, \pm 1$. The states $F_z = 0$ and ± 1 of the $J=3/2$ branch are given a subscript L while those of the $J=1/2$ branch are given a subscript U. The

hole states are usually labeled L_J with the J value of the angular momentum and the angular momentum of the envelope function. The single particle wave function for the hole then takes the form:

$$\psi_h^{L_J}(\mathbf{r}) = R^h(\mathbf{r}) u_{J,M_z}(\mathbf{r}) \quad (2)$$

In the fine structure model used here, only S hole states, $S_{1/2}$ and $S_{3/2}$ appear since the envelope function is restricted to $L=0$ states. The P hole states give rise to exciton that fall outside of the laser band width for the QD sizes considered in the experiments.

The EMA and $\mathbf{k} \cdot \mathbf{p}$ parabolic expansion at the Γ point of the Brillouin zone provide a one particle Schrödinger equation for the radial envelope functions. Using a finite depth spherical confinement potential, one gets specific effective masses for the different states of the hole and the electron inside and outside the spherical well.³ The model parameters were determined using spherical wells for the confinement potential (particle in a sphere, PS) for the hole and the electron (see for example ref. ⁴).

$$H_i R_i(\mathbf{r}) = \left(-\frac{\hbar^2}{2} \nabla \frac{1}{m_i(\mathbf{r}_i)} \nabla + V_i(\mathbf{r}_i) \right) R_i(\mathbf{r}) = E_i R_i(\mathbf{r}), \quad i=e,h \quad (3)$$

which can be solved implicitly to get the eigen function $R_i(\mathbf{r})$ and E_i . $V_i(\mathbf{r}_i)$ is the confining spherical potential of radius a

$$V_i(r) = \begin{cases} 0 & r < a \\ V_i^0 & r > a \end{cases} \quad (4)$$

The effective mass of the hole or the electron inside the QD are $m_e^* = 0.13$ and $m_h^* = 0.82$ for the electron and the hole, respectively. The effective mass outside the QD is taken equal to 1. The depth of the confinement potentials depend on the QD size and were estimated from the empirical relation given in ref.⁵: $V_0^e(a) = 3.49 + 2.47(2a)^{-1.32}$, $V_0^h(a) = 5.23 + 0.74(2a)^{-0.95}$. The term V_{eh} is the diagonal (first order in perturbation theory) Coulomb attraction between the hole and the electron wave function. It is computed as in ref. ⁴.

The energy of an exciton band takes the form:

$$E_{exciton} = E_e - E_h + E_{gap} + V_{eh} \quad (5)$$

where E_{gap} is the bulk value for CdSe (= 1.75 eV). E_e and E_h are computed by solving the Schrödinger equation Eq. (3) for the electron and the hole.

Excitons are labeled by the angular momentum of the radial envelope function, L , and the spin state, s , of the Bloch function for the hole and the electron, $L_s^h - L_s^e$. The ground state exciton (lowest electronic excited state) is labeled $1S_{3/2}^h - 1S_{1/2}^e$. Here we consider two hole states and one electron state, which leads to four exciton bands : $1S_{3/2}^h - 1S^e$, $1S_{1/2}^h - 1S^e$, $2S_{3/2}^h - 1S^e$ and $2S_{1/2}^h - 1S^e$ where we dropped the s value for the electron because it is $1/2$ throughout.

The validity of the PS model for the value of the energy of ground state exciton, $1S_{3/2}^h - 1S^e$ (Eq. (5)) was checked with respect to results available in the literature that are plotted in Figure S2.1.

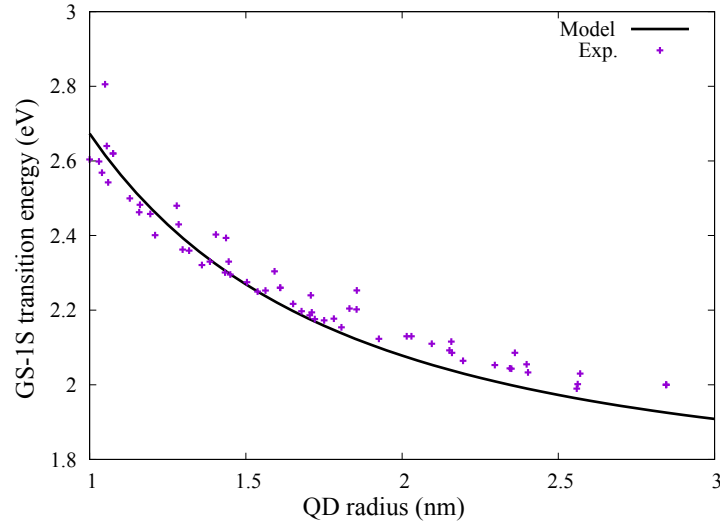


Figure S1.1. Comparison between the energy of the $GS-1S_{3/2}^h - 1S^e$ transition computed using Eq. (5) and experimental values of the energy for the lowest absorption band of CdSe QD of radius ranging from 1 and 3 nm taken from the refs.⁵⁻⁹

The PS model is known to be less accurate for larger QD sizes where interband mixing starts to be important.^{1,10} The computed value for $GS-1S_{3/2}^h - 1S^e$ transition the QD of 3.3 nm (1.75 nm radius) is in good agreement with the experimental data of Figure S1.1. For the larger QD of 4.4 nm, the value is underestimated. In order to get a correct fit of the absorption spectrum shown in Figure 1d, we took a QD diameter of 3.9 nm (radius of 1.95 nm) for the model results which is well within the width of the size dispersion histogram reported in Figure 2(f). The simple PS model also significantly over estimates the energy of the excited exciton band 2S which involves the first excited hole state. Moreover, accurate spectroscopic data for excited excitons are scarcer. The discrepancy arises both from neglecting off diagonal Coulomb interactions and band mixing. For fitting the absorption spectra

of Figure 2(a) and (d), the value of the energy difference between the two lowest excitons was therefore taken from a fit to the spectroscopic data of ref.¹¹.

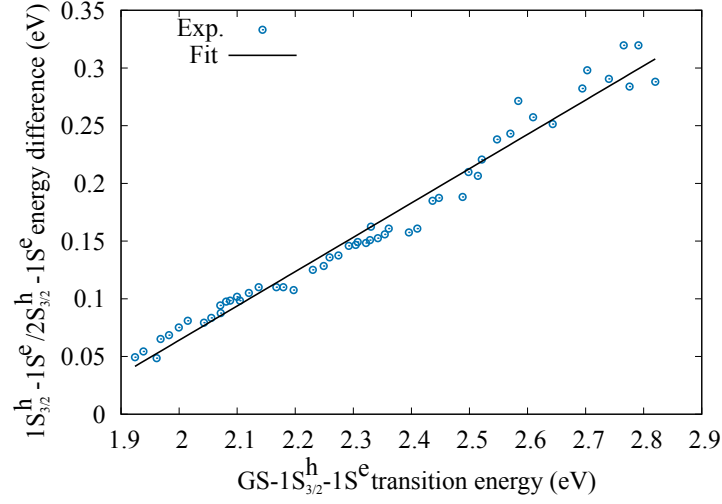


Figure S1.2. Experimental energy difference between first ($E_1=1S_{3/2}^h-1S^e$) and second absorption maxima ($E_2=2S_{3/2}^h-1S^e$) of CdSe QD of different radius as a function of the absolute value of the maximum absorption of the first maximum. Extracted and adapted from Norris and Bawendi.¹¹ The black line is the linear fit is the linear fit ($E_2 - E_1 = -0.524 + 0.294 \times E_1$) in the E_1 range [1.9-2.9] eV.

The two fitted energies for the $1S_{3/2}^h-1S^e$ and $2S_{3/2}^h-1S^e$ excitons were then used to build the fine structure matrix that includes the SO coupling and therefore also the higher spin bands ($S=1/2$) of the hole states, leading to two more excitons bands : the $1S_{1/2}^h-1S^e$ and the $2S_{1/2}^h-1S^e$. So in total we have we have 8 degenerate states for the $1S_{3/2}^h-1S^e$ and 4 degenerate states for the $1S_{1/2}^h-1S^e$ that can be split by spin-orbit, exchange and crystal field interactions. The same is true for the 2S exciton bands. The spin orbit interaction can only couple states that corresponds to triplet and singlet electronic configurations.¹² The matrix of the manifold of 12 states, ordered as a function of the F_z projection values : -2, +2, -1, +1, 0 as in ref.¹² is shown in Table S1.1 for the 1S excitonic band and on Table S1.2 for the 2S excitonic band. The values of the parameters used for the coupling are given in Table S1.3. The value of the SO coupling was obtained from fitting the experimental absorption spectra of QD of 3.3 and 4.4 nm of Figure 2. As explained in the main text, the obtained value for the SO coupling is 220 meV, about half of the bulk value. A computational study on the effect of SO in Si nanocrystal shows that the strength of the coupling decreases with the radius of the QD.¹³ The gap

between the $1S_{1/2}$ and the $2S_{3/2}$ bands decreases with the value of the SO coupling. Systematic modeling studies show these two bands can cross for low values,¹⁴ see also ref.¹⁵ for CdS nanocrystals. The set of parameters reported in Table S2.3 is valid for the absorption spectra measured in range of diameters 3.3 to 4.9 nm.

The exciton transition dipoles, $\langle R^h(\mathbf{r}) | \mathbf{r} | R^e(\mathbf{r}) \rangle$, where $\mathbf{r}$ is the particle coordinate, were computed numerically using the wave functions of the hole and the electron, obtained by Eq. (3) as a function of the QD radius, Figure S1.3 for the 1S and 2S exciton bands. The states of the 1S band are about twice brighter than the states of the 2S band. In each band, the states of the $S_{3/2}$ manifold with $F_z = \pm 2$ and 0^L are dark. Transition dipole moments of 1S and 2S bands are redistributed over all bright excitons of the fine structure based on their coefficients after diagonalization.

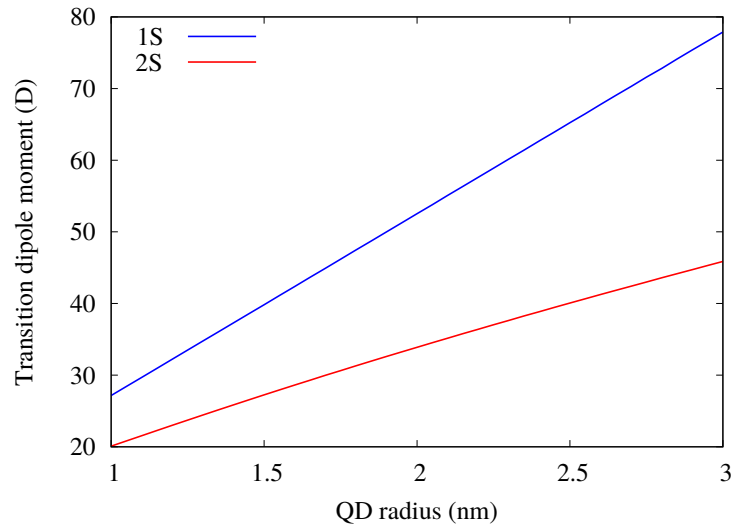


Figure S1.3. Computed transition dipoles of the 1S and 2S using the PS model as a function of the QD size.

Table S1.1. Model exciton Hamiltonian, 1S.

	1	2	3	4	5	6	7	8	9	10	11	12
1	A1											
2		A1										
3			B1	X1	X1							
4			X1	C1	Y1							
5			X1	Y1	D1							
6						D1	X1	X1				
7						X1	B1	Y1				
8						X1	Y1	C1				
9									E1	X1	X1	
10									X1	F1		X1
11									X1		D1	Y1
12										X1	Y1	E1

Table S1.2. Model exciton Hamiltonian, 2S.

	13	14	15	16	17	18	19	20	21	22	23	24
13	A2											
14		A2										
15			B2	X2	X2							
16			X2	C2	Y2							
17			X2	Y2	D2							
18						D2	X2	X2				
19						X2	B2	Y2				
20						X2	Y2	C2				
21									E2	X2	X2	
22									X2	F2		X2
23									X2		D2	Y2
24										X2	Y2	E2

Where:

$$\begin{aligned}
A1 &= E_1 - \frac{\Delta_{SO}^{1S}}{3} - 3K & /B1 &= E_1 - K & /C1 &= E_1 - 3K \\
D1 &= E_1 - 3K + \Delta_{xf} & /E1 &= E_1 + \frac{\Delta_{SO}^{1S}}{3} - 3K & /F1 &= E_1 - K + \Delta_{xf} \\
A2 &= E_2 - \frac{\Delta_{SO}^{2S}}{3} - 3K & /B2 &= E_2 - K & /C2 &= E_2 - 3K \\
D2 &= E_2 - 3K + \Delta_{xf} & /E2 &= E_2 + \frac{\Delta_{SO}^{2S}}{3} - 3K & /F2 &= E_2 - K + \Delta_{xf} \\
Y1 &= -\frac{\Delta_{SO}^{1S}}{3} & /X1 &= -\frac{\Delta_{SO}^{1S}}{3} & / & \\
Y2 &= -\frac{\Delta_{SO}^{2S}}{3} & /X2 &= -\frac{\Delta_{SO}^{2S}}{3} & / &
\end{aligned}$$

Table S1.3. Parameters used for modeling the fine structure.

QD	A	B	
D	3.3	4.4(3.9)	nm
Δ_{SO}^{1S}	220	220	meV
Δ_{SO}^{2S}	220	220	meV
Δ_{xf}	25	25	meV
K	12	12	meV

S1.2 Absorption spectra

The eigen energies of the fine structure excitons are obtained by diagonalization of the matrices of Tables S1.1 and S1.2 and the oscillator strengths of the bright eigenstates from the eigenvectors. These provide stick spectra shown in Figures 2(a) and 1(d) and the level structures shown in Figure 1 of the main text and in the right panels of Figures S1.4 and S1.5. The absorption spectra of Figure 2(a) and 1(d) are obtained by convoluting the stick spectra with a Gaussian of FWHM of 0.08 eV.

The projection quantum number F_z is conserved upon diagonalization but because of the spin orbit and the exchange interaction, rigorously, the zero order spin label $3/2$ and $1/2$ is lost. However, as shown in scheme 1 and in Figures S1.4 and S1.5, for each S band, groups of eigenstates have energies that correspond to the energy of the $S_{3/2}$ and $S_{1/2}$ zero order (zo) states. We therefore kept this labeling in Figure 1 and in Figure 2, as is typically done in the assignment of spectroscopic data. The 8 lowest energy eigenstates fall in the $S_{3/2}$ energy range. The lowest ones (1 and 2) have F_z values equal to -2

and +2. They are not mixed by the SO or the exchange interactions. Their energies correspond to the z_0 energies. The next pair of degenerate eigenstates have values of $F_z = -1$ and $+1$. They are superpositions of the three zero order eigenstates of the $F_{zv} = -1$ and $F_z = +1$ manifolds, respectively. Their main weight is on the zero order $S_{3/2}$ excitons (i.e., z_0 states 4 and 8 in Table S1.3 which belong to the L branch (from $F=2$)). The next eigenstate belongs to $F_z = 0$, it is a mixture of the z_0 exciton 9 ($S_{1/2}$) and 10 and 11 (both $S_{3/2}$) with its main weight on exciton 11 (L branch of $F=0$). Next comes a degenerate pair of $F_z = -1$ and $F_z = +1$ eigenstates, superpositions with equal weights of the $S_{1/2}$ and $S_{3/2}$ excitons (z_0 excitons 3, 5 and 6,7 respectively). The highest eigenstate is $F = 0$. It is a superposition of z_0 states 9 ($S_{1/2}$), 10 ($S_{3/2}$) and 12 ($S_{1/2}$) with the highest weight on state 10 (L branch). The 4 highest eigenstates have energies that fall in the range of the $S_{1/2}$ z_0 states. They are however all of mixed $S_{1/2}$ and $S_{3/2}$ character. The lowest state of this manifold has $F_z = 0$, with equal weights on z_0 states 9, 10 and 12. Next is a pair of $F_z = -1$ and $F_z = +1$ degenerate eigenstates, with equal weights on z_0 states 3, 4, 5 and 6, 7, 8 respectively. The highest state is $F_z = 0$ with equal mixtures of z_0 states 9, 11 and 12.

Because the value of the SO coupling between the $S_{3/2}$ and $S_{1/2}$ bands is larger than the energy difference between the 1S and the 2S exciton bands, for the range of QD size investigated, one obtains the order shown in Scheme 1 for the eigen states: a band of 8 states in the range of $1S_{3/2}$, a band of 8 states in the range of $2S_{3/2}$ and then two bands of 4 states in the range of $1S_{1/2}$ and $2S_{1/2}$.

S1.3 Assignment of modeled coherences

The transition energies between the different bands of eigenstates lead to the spectra of the transition frequencies plotted in the left panels of Figures S1.4 and S1.5 for the 3.3 and 4.4 nm QD, respectively. Based on the analysis given above in Section S2.2, one can label the transitions frequencies according to an intra-band and inter-band character.

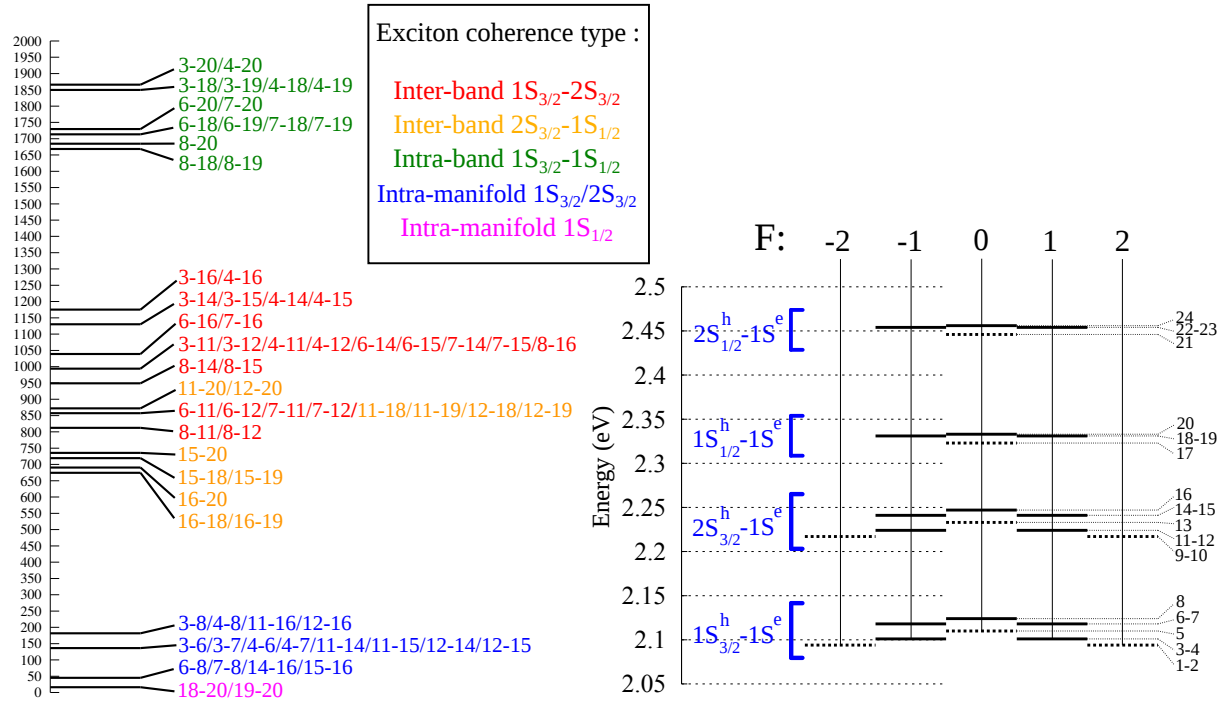


Figure S1.4. Energy gaps involved in the bright transitions between fine structure levels in CS3.3, calculated using the energies reported in the inset (the 24 fine levels are labeled by increasing energy from 1 to 24.). The transitions are color-coded as intra-band $1S_{1/2}$ (magenta); intra-band $1S_{3/2}$ and $2S_{3/2}$ (blue); intra-band $1S_{3/2}$ and $1S_{1/2}$ (green); inter-band $2S_{3/2}-1S_{1/2}$ (yellow) and $1S_{3/2}-2S_{3/2}$ (red). Close to each line, the pairs of states (i-j, with i and j ranging from 1 to 24) separated by that specific energy gap are reported.

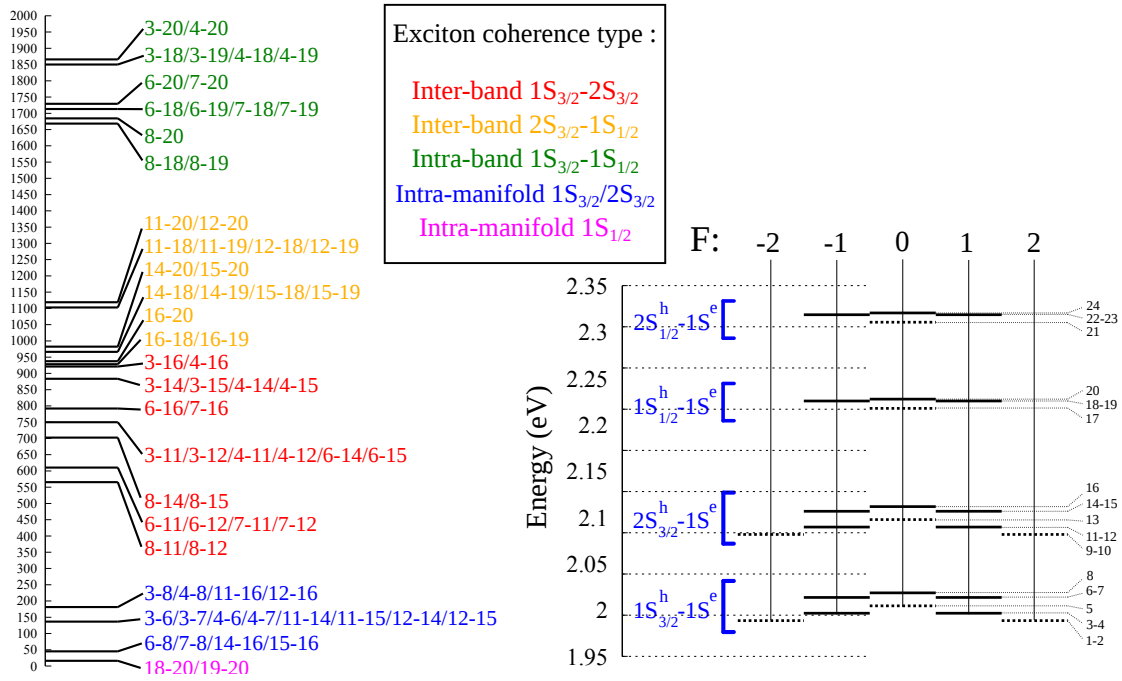


Figure S1.5. Energy gaps involved in the bright transitions between fine structure levels in CS4.4, estimated using the energies reported in the inset (the 24 fine levels are labeled by increasing energy from 1 to 24.). The transitions are color-coded as intra-band $1S_{1/2}$ (magenta); intra-band $1S_{3/2}$ and $2S_{3/2}$ (blue); intra-band $1S_{3/2}$ and $1S_{1/2}$ (green); inter-band $2S_{3/2}-1S_{1/2}$ (yellow) and inter-band $1S_{3/2}-2S_{3/2}$ (red). Close to each line, the pairs of states (i-j, with i and j ranging from 1 to 24) separated by that specific energy gap are reported.

S2. 2DES measures

S2.1 Pulse characterization

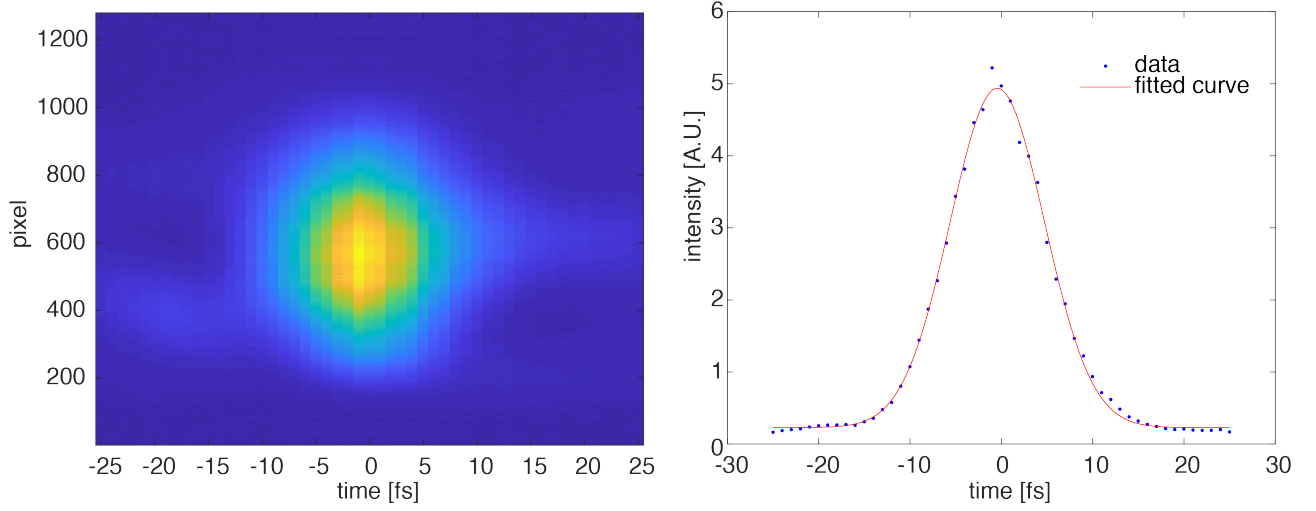
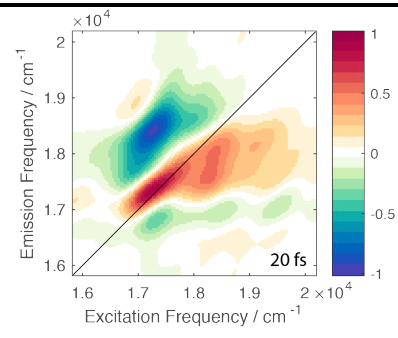
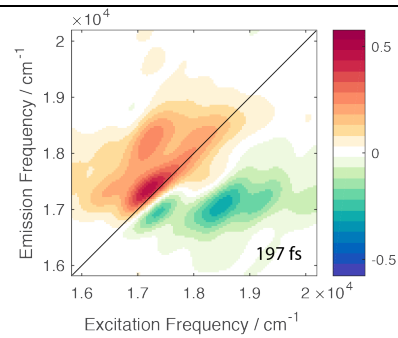
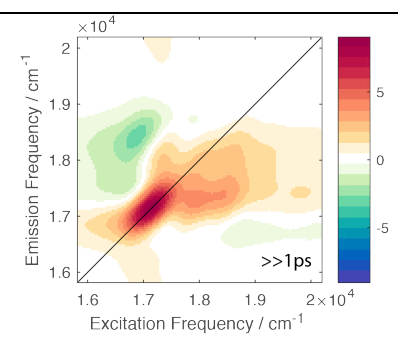
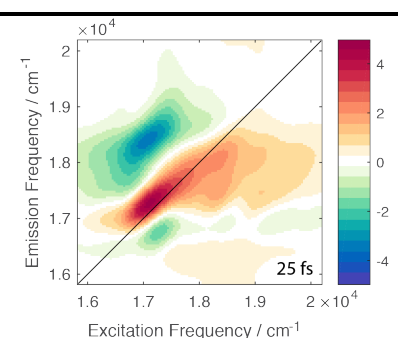


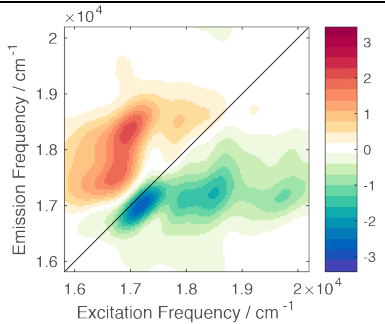
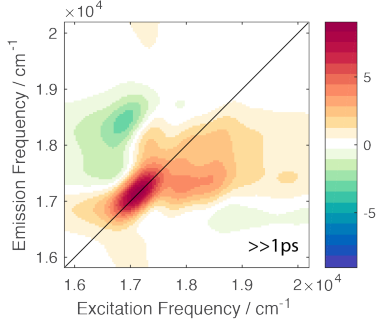
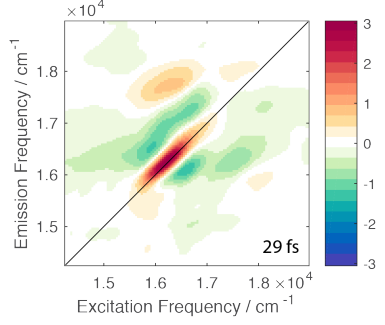
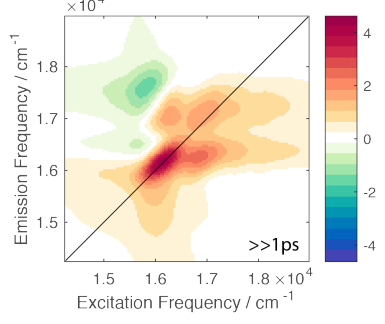
Figure S2.1. FROG measurement at the sample position in a 1mm cuvette filled with dimethylsulphoxide (laser profile of Figure 2(d)). The pulse duration is estimated to be 8 fs.

S2.2 Data analysis

The datasets are analyzed with a global complex multi-exponential fit method as proposed in ref. ^{16,17}. Briefly, the decay of the total complex signal at each point of the 2D map is fitted with a global function written as a sum of complex exponentials: $f = \sum_{n=1}^N a_n e^{i\phi_n} e^{-t_2/\tau_n} e^{-i\omega_n t_2}$. Components with $\omega_n = 0$ describe population decay contributions, whereas components with $\omega_n \neq 0$ represent oscillating components associated to coherent dynamics along t_2 . The corresponding amplitude a_n plotted in a 2D map as a function of ω_1 and ω_3 builds the so-called DAS (decay associated spectra) and CAS (coherence associated spectra), respectively. These maps allow the direct visualization of the sign and the amplitude distribution of a particular decay component along the 2D spectra. Given the n -th component associated to the time constant τ_n , a positive amplitude is found at positions in the 2D maps where the signal is decaying with τ_n , whereas a negative amplitude is found where the signal is rising with τ_n . Note that with this methodology it is possible to directly extract the time constants regulating the population dynamics but also the dephasing time and phase of the beating contributions.

Table S2.1. Population dynamics parameters from the global fitting applied on 2DES data of the different samples considered in this work. The first 10 fs have been discarded from the fitting.

<i>sample</i>	<i>component</i>	<i>Time constant</i>	<i>Physical interpretation</i>	<i>DAS</i>
CS3.3-MPA water	1	20 fs	hot carrier relaxation, spectral diffusion, scattering	
	2	197 fs	Inter-band relaxation and/or surface related relaxation channels	
	3	>>1ps	Relaxation dynamics of the lowest energy exciton	
CS3.3-MUA water	1	25 fs	hot carrier relaxation, spectral diffusion, scattering, pulse overlap effects	

CS4.4- TOPO hexane	2	305 fs	Inter-band relaxation and/or surface related relaxation channels	
	3	>>1ps	Relaxation dynamics of the lowest energy exciton	
	1	29 fs	hot carrier relaxation, spectral diffusion, scattering	
	2	>1ps	Relaxation dynamics of the lowest energy exciton	

S2.2 Additional 2DES data

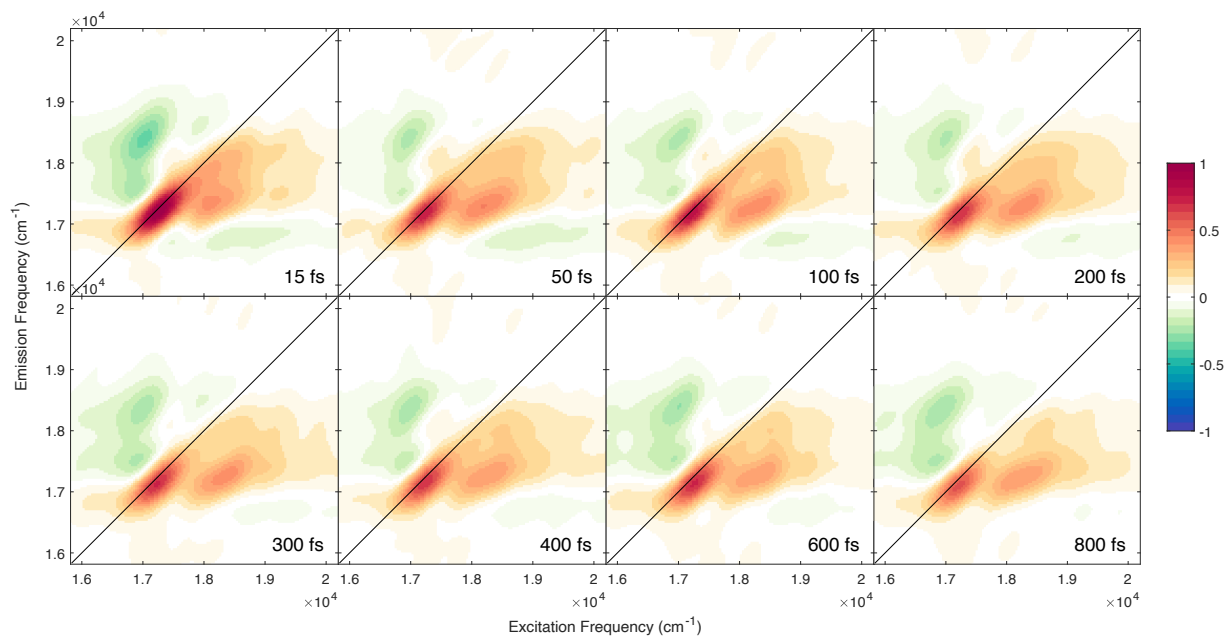


Figure S2.2. Rephasing 2DES data of CS3.3-MPA in water.

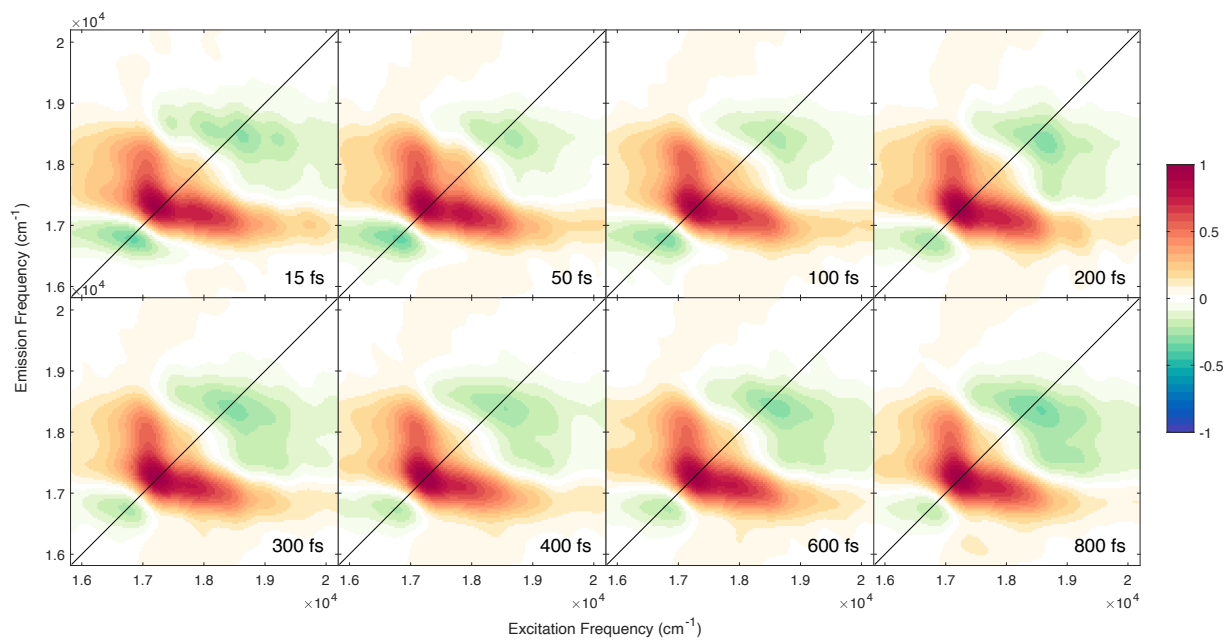


Figure S2.3. Non-rephasing 2DES data of CS3.3-MPA in water.

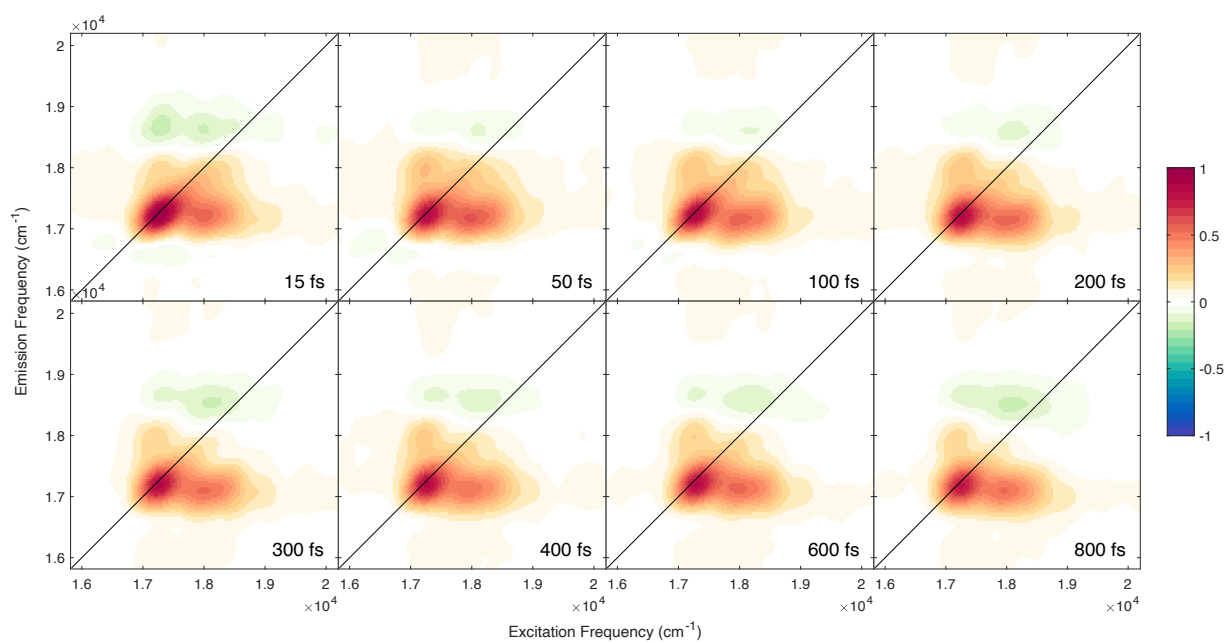


Figure S2.4. Total (pure absorptive) 2DES data of CS3.3-MPA in water.

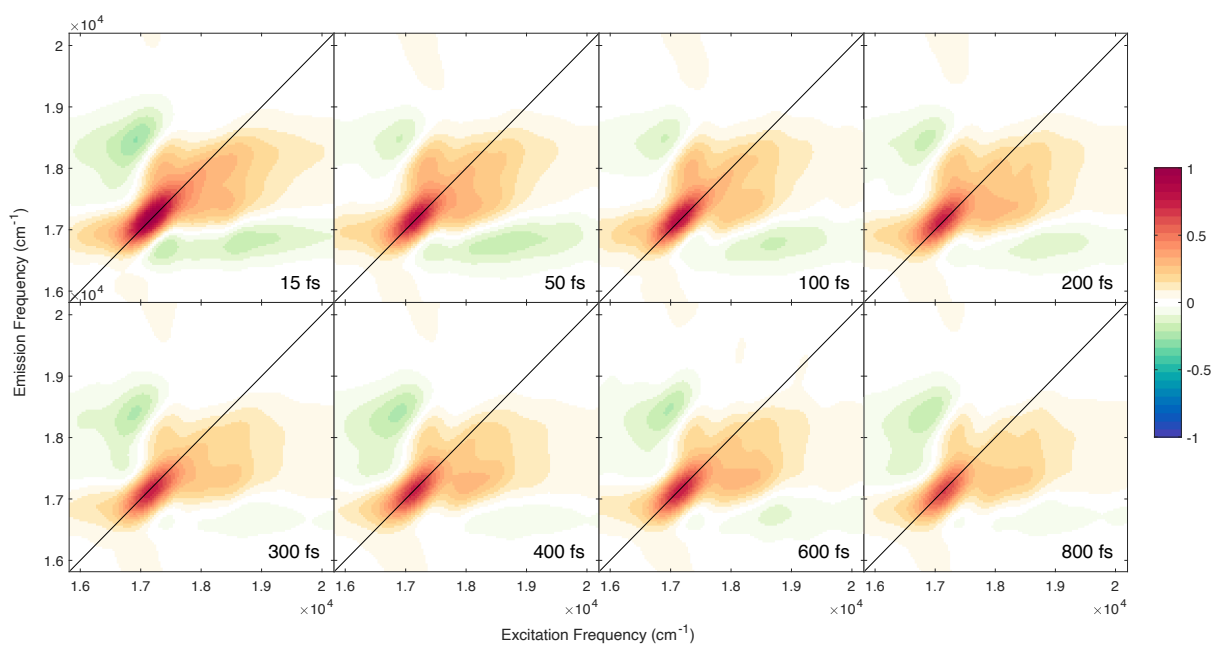


Figure S2.5. Rephasing 2DES data of CS3.3-MUA in water.

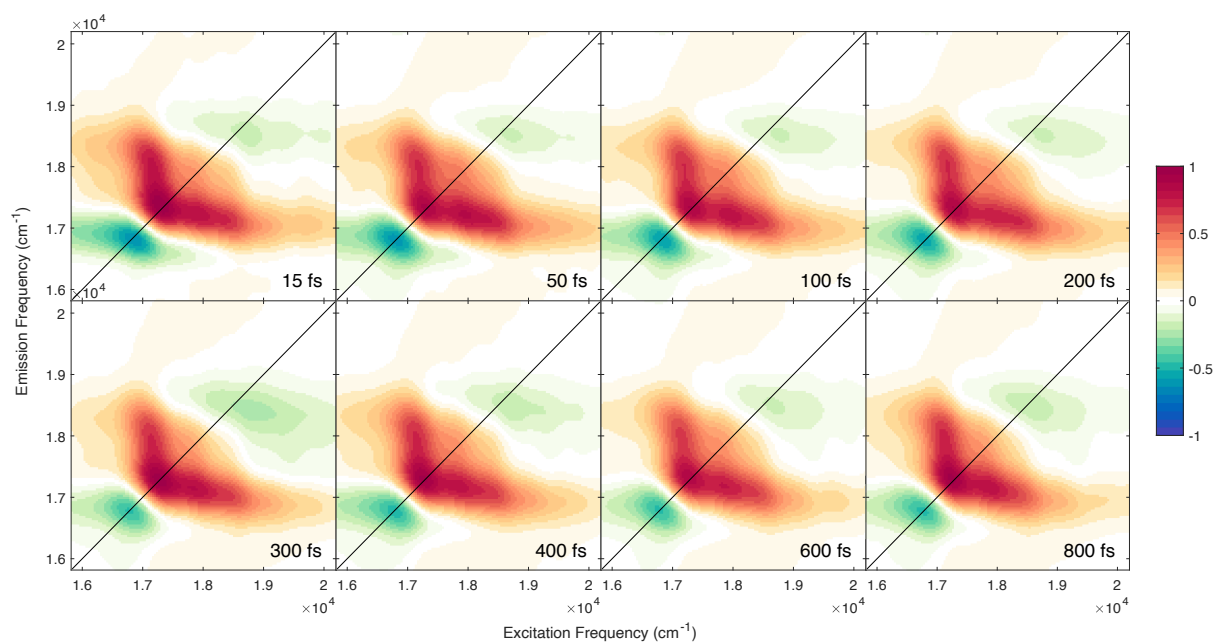


Figure S2.6. Non-rephasing 2DES data of CS3.3-MUA in water.

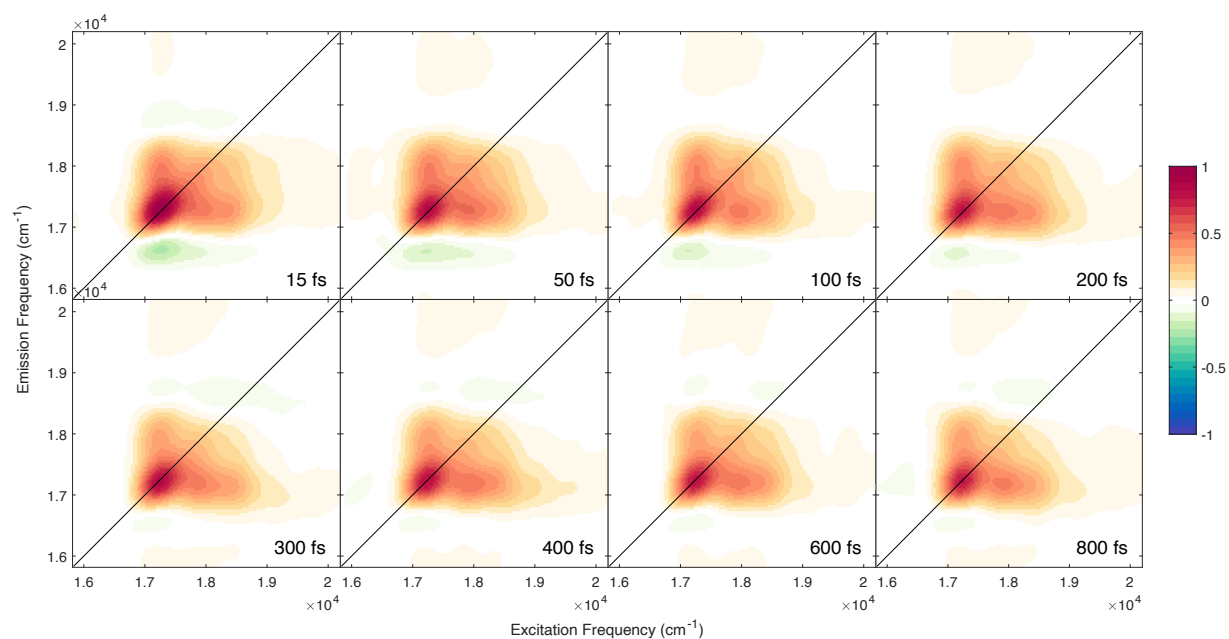


Figure S2.7. Total (pure absorptive) 2DES data of CS3.3-MUA in water.

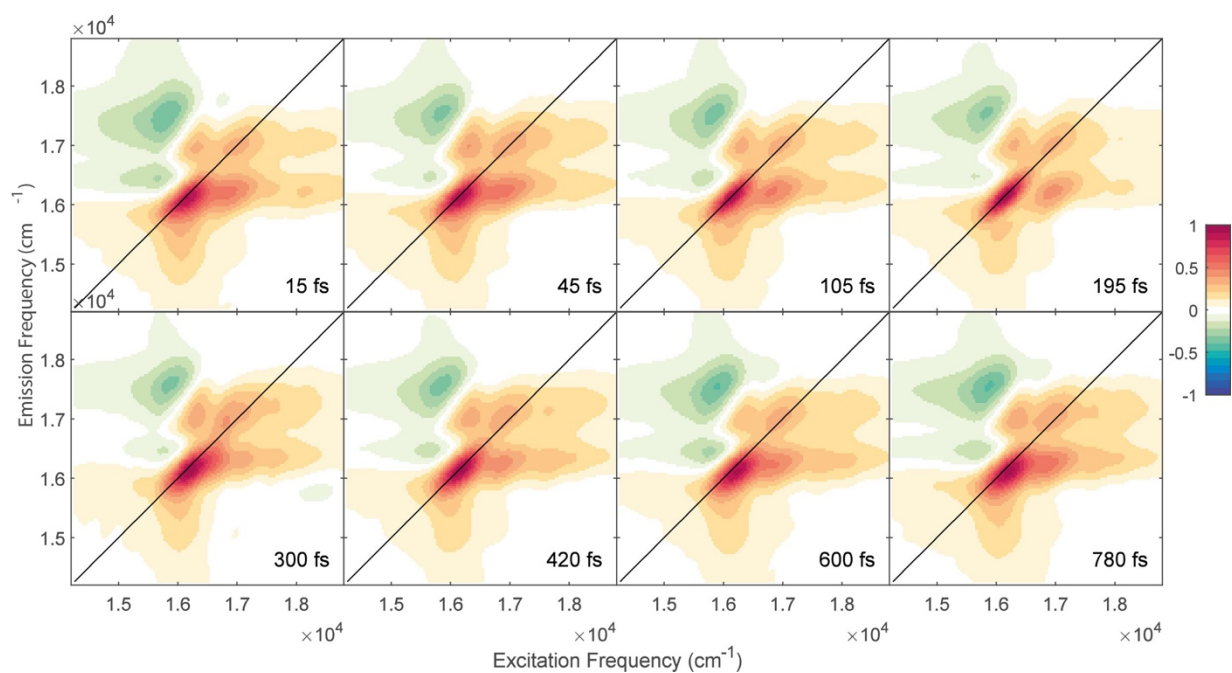


Figure S2.8. Rephasing 2DES data of CS4.4-TOPO in hexane.

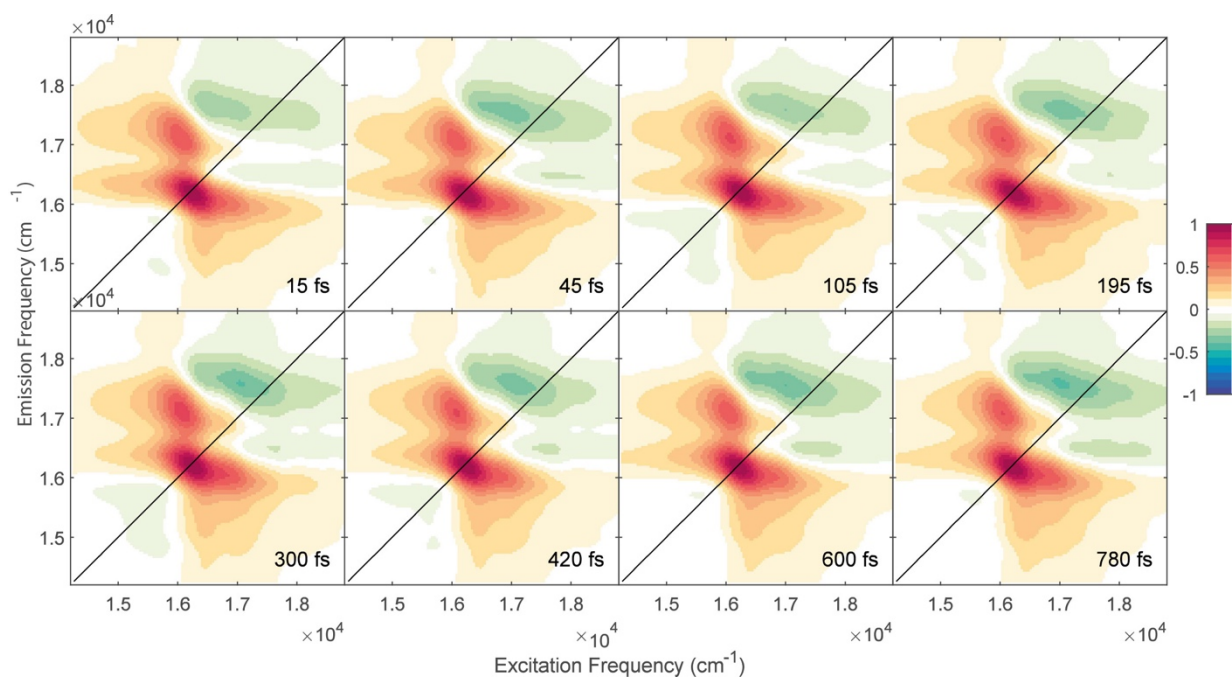


Figure S2.9. Non-rephasing 2DES data of CS4.4-TOPO in hexane.

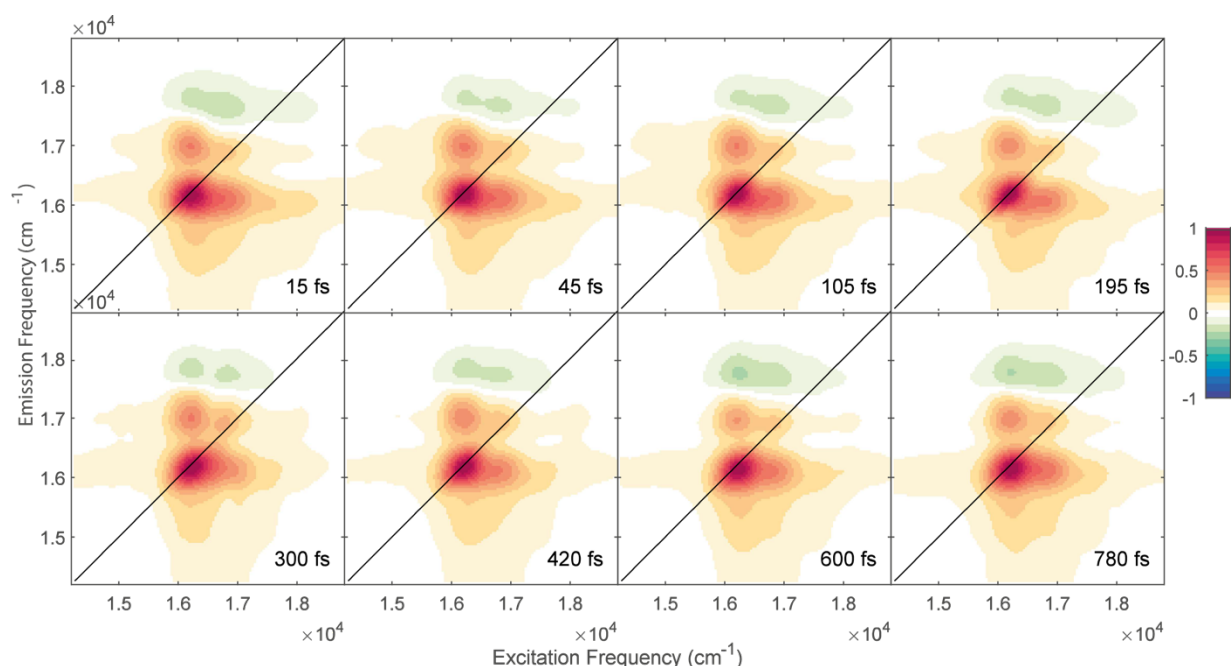


Figure S2.10. Total (pure absorptive) 2D data of CS4.4-TOPO in hexane.

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